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## Disorder-induced solitons in conjugated polymers

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**Abstract.** – We show that weak off-diagonal disorder in degenerate ground-state conjugated polymers results in a finite density of randomly positioned kinks (solitons and antisolitons) in the lattice dimerization. For realistic values of the disorder, these kinks should clearly show up in the optical and magnetic properties.

For over thirty years, conjugated polymers have provided a rich field of fundamental and technological research [1], [2]. The electrons in these organic materials propagate mostly along chains formed by carbon atoms. Conjugated polymers belong to a large class of quasi-one-dimensional Peierls insulators, in which a periodic chain distortion results from the interaction of the lattice with the itinerant electrons [3]. Much attention has been devoted to trans-polyacetylene, which has a doubly degenerate ground state. The degeneracy allows for topological excitations, solitons, which are kinks in the lattice dimerization accompanied by a local distortion of the electron density [1]. Solitons provide a simple explanation of the unusual properties of doped trans-polyacetylene [1], [2]. They also feature in quantum lattice fluctuations, which lead to subgap optical absorption [4] and may be responsible for an enhanced nonlinear optical response [5]. Solitons were first found in the free-electron Su-Schrieffer-Heeger (SSH) model [1], [6]. Their topological nature, however, allows them to survive also in the presence of on-site Coulomb repulsion (Peierls-Hubbard model) [7].

Although real polymer materials contain many types of defects, most theoretical studies have been restricted to perfect chains. Due to the quasi-one-dimensional nature of polymers, however, any disorder will play a major role in determining their properties. In this letter, we study the effects of weak disorder in the electron hopping amplitudes in polyacetylene chains. Such (off-diagonal) disorder arises from random chain twists that diminish the overlap between the  $\pi$ -orbitals of neighboring carbon atoms. In previous analytical studies, off-diagonal disorder was modeled by small fluctuations of the Peierls order parameter around an average value [8], [9]. Numerical calculations showed, however, that if the lattice configuration of

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a weakly disordered chain described by the SSH model is allowed to relax, it may contain solitons, *i.e.* large (nonperturbative) variations of the order parameter [10], [11]. This implies that the lattice response to the disorder cannot be neglected. An analytical theory for this phenomenon and an estimate (either numerical or analytical) for the density of thus created kinks have so far not been given. In this letter, we address these issues and we show that, in fact, arbitrarily small off-diagonal disorder leads to a finite density of solitons. Our arguments also hold in the presence of electron correlations.

We consider a half-filled chain, in which itinerant ( $\pi$ ) electrons interact with the classical carbon lattice. We assume that the chain Hamiltonian contains three contributions: i) the electron hopping between adjacent carbon atoms, ii) the elastic energy of the lattice, and iii) the Coulomb repulsion between the electrons. The hopping amplitude has the form

$$t_{m,m+1} = t_0 + \alpha(u_m - u_{m+1}) + \delta t_{m,m+1}. \quad (1)$$

Here the first term is the bare amplitude and the second term describes the electron-phonon interaction, where  $\alpha$  is the coupling constant and  $u_m$  denotes the displacement of the  $m$ -th carbon atom from its uniform-lattice position. Finally, the third term is a random contribution, which we include to describe the conformational disorder. We assume that the fluctuations  $\delta t_{m,m+1}$  are frozen ("quenched" disorder) and that they are independent for different links. We will restrict ourselves to zero-temperature properties.

As we shall shortly see, for weak disorder the spatial extension of a disorder fluctuation necessary to create a kink is much larger than one lattice unit, which allows us to use a continuum model. Then eq. (1) is replaced by

$$\Delta(x) = \Delta_{\text{lat}}(x) + \eta(x), \quad (2)$$

where the lattice dimerization  $\Delta_{\text{lat}}(2am) = \alpha(u_{2m-1} - 2u_{2m} + u_{2m+1})$  ( $a$  is the lattice constant) describes the alternating part of the hopping amplitude determined by the shifts  $u_m$  of the carbon atoms (cf. the continuum version of the SSH model [12]) and  $\eta(2am) = \delta t_{2m-1,2m} - \delta t_{2m,2m+1}$  describes the disorder part with a Gaussian correlator,

$$\langle \eta(x)\eta(y) \rangle = A\delta(x-y). \quad (3)$$

Note that, while chain twists always decrease, the hopping amplitudes ( $\delta t_{m,m+1} < 0$ ),  $\eta(x)$  can be both positive and negative, as it is the alternating part of the fluctuations.

It should now be realized that in a consistent treatment of disorder,  $\Delta_{\text{lat}}(x)$  implicitly depends on the  $\eta(x)$ . The reason is that at zero temperature  $\Delta_{\text{lat}}(x)$  for a particular disorder realization is found by minimizing the total (electronic plus lattice) energy. Treating the lattice classically, the total energy reads

$$E = E_{\text{el}}[\Delta(x)] + \frac{1}{\pi\lambda v_F} \int dx \Delta_{\text{lat}}^2(x), \quad (4)$$

where  $\lambda = 4\alpha^2/\pi t_0 K$  is the dimensionless electron-phonon coupling constant ( $K$  is the spring constant),  $v_F = 2at_0$  is the bare value of Fermi velocity, and we set  $\hbar = 1$ . The electron energy depends on  $\Delta(x)$  defined by eq. (2), which includes the changes of the hopping amplitudes due to both the lattice distortion and the disorder. Equation (4) can be derived in immediate analogy with the continuum version of the SSH model [12]. The difference is that in our case  $E_{\text{el}}[\Delta(x)]$  also contains the off-diagonal disorder and the electron-electron interaction. In what follows, we will not need an explicit expression for the electron energy, provided that it satisfies two important conditions. First, in the absence of disorder the total energy of a half-filled chain should have two minima, both corresponding to a uniform dimerization,  $\Delta(x) = \pm\Delta_0$ . Second, we will assume that the model admits soliton solutions, *i.e.* apart from the above minima, the

total energy has an infinite number of extrema  $\Delta_N(x|\mathbf{z})$  corresponding to the presence of  $N$  kinks (solitons and antisolitons interpolating between  $-\Delta_0$  and  $+\Delta_0$  and vice versa), whose positions are described by the  $N$ -dimensional vector  $\mathbf{z} = (z_1, z_2, \dots, z_N)$ . Both the SSH and the Peierls-Hubbard model have these properties. If the average separation between neighboring kinks is large compared to the correlation length  $\xi_0 = v_F/\Delta_0$ , the configuration with  $N$  kinks has energy

$$E_N = E_0 + N E_s, \quad (5)$$

where  $E_s$  is the energy needed to create a single soliton. The kinks can be either charged and spinless or neutral with spin  $\frac{1}{2}$  [1]. In the SSH model, the two types have the same energy, while in the presence of Coulomb repulsion the neutral soliton is energetically favorable [7], [13] and in undoped chains will be the only type of kink that occurs at zero temperature.

At weak disorder,  $|\eta(x)| \ll \Delta_0$ , linear-response theory predicts small fluctuations of the ground-state lattice configuration around the uniformly dimerized lattice. We will show, however, that for arbitrarily weak disorder the ground-state configuration cannot be found using linear-response theory, as the configuration with small fluctuations around a chain containing a number of solitons may have a lower energy than the one with small fluctuations around uniform dimerization.

To first order in  $\eta(x)$ , the correction to the energy of a multikink configuration reads

$$\delta E_N = -\frac{2}{\pi \lambda v_F} \int dx \Delta_N(x|\mathbf{z}) \eta(x), \quad (6)$$

where the extremum condition for the ordered configuration  $\Delta_N(x|\mathbf{z})$  was used. From eq. (6) the change of the total energy of the uniformly dimerized state ( $\Delta(x) = \Delta_0$ ) due to disorder is obtained:

$$\delta E_0 = -\frac{2\Delta_0}{\pi \lambda v_F} \int dx \eta(x). \quad (7)$$

Consider now, on the other hand, the same chain with an antisoliton at  $z_1$  and a soliton at  $z_2$ , chosen in such a way that the whole disorder fluctuation lies between  $z_1$  and  $z_2$ . The change of energy due to disorder for this configuration equals  $-\delta E_0$ , because between  $z_1$  and  $z_2$   $\Delta_2(x|z_1, z_2) \approx -\Delta_0$ . We thus find that in the disordered chain, the configuration with a soliton-antisoliton pair is energetically favorable to the uniform configuration if

$$-\int dx \eta(x) > \gamma \lambda v_F. \quad (8)$$

Here  $\gamma = \pi E_s/2\Delta_0$ , which in the case of the SSH model equals 1. It should be stressed that as long as the kink density is indeed small compared to  $1/\xi_0$ , the entire effect of electron-electron interactions is contained in the factor  $\gamma$ . We note that, no matter how small the disorder is, the fluctuations in  $\int dx \eta(x)$  grow with the chain size, so that for a sufficiently long chain the inequality eq. (8) will certainly be fulfilled.

The creation of kinks by off-diagonal disorder is illustrated in fig. 1. The thick line is the ground-state order parameter  $\Delta_m \equiv \Delta(2am) = t_{2m-1,2m} - t_{2m,2m+1}$  for a discrete chain of 160 carbon atoms, obtained by numerically minimizing the total energy for one particular realization of the disorder. In this example, we neglected the Coulomb repulsion and used standard SSH parameters [1]. It is clearly seen that the order parameter fluctuates near a soliton-antisoliton pair configuration. The disorder realization that was used as input is visualized by the thin line, which gives  $\Delta_0 + \eta_m = \Delta_0 + \delta t_{2m-1,2m} - \delta t_{2m,2m+1}$  ( $\Delta_0 \approx 0.7$  eV). The thin line in fact directly represents the order parameter along the chain if we neglect the lattice relaxation. In that case, no lattice kinks are created.

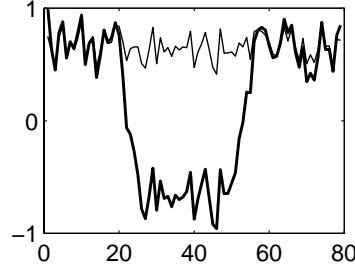


Fig. 1. – Numerically obtained order parameter along a polyacetylene chain of 80 pairs of carbon atoms for one particular (but typical) realization of off-diagonal disorder. The thin line does not account for lattice relaxation, the thick line does.

In order to obtain an estimate for the density of disorder-induced kinks, we consider a disorder fluctuation with spatial size  $l$  and constant value  $\eta_l$ . Then, according to eq. (8), the threshold for the creation of a soliton-antisoliton pair is

$$|\eta_l| = \frac{\gamma \lambda v_F}{l}. \quad (9)$$

By requiring the probability density of such a fluctuation,

$$p = \exp \left[ -\frac{1}{2A} \int dx \eta(x)^2 \right] = \exp \left[ -\frac{(\gamma \lambda v_F)^2}{2Al} \right], \quad (10)$$

to be of the order of unity, we obtain the average density of kinks:

$$n = \frac{1}{l} = \frac{A}{(\gamma \lambda v_F)^2}. \quad (11)$$

The condition  $p \sim 1$  ensures that the typical value of  $\int_x^{x+l} dx' \eta(x')$  is large enough to stabilize a soliton-antisoliton pair. The probability to find such a pair with separation much smaller than the average given by eq. (11) is suppressed (cf. eq. (10)) as it requires a large disorder fluctuation. On the other hand, lattice configurations in which the average distance between the kinks is significantly larger than  $l$  given by eq. (11) are statistically less likely. Similar arguments were used to estimate the typical domain size for the Ising model in a random magnetic field [14]. The analogy is not accidental: it can be shown that the statistical properties of the disorder-induced kinks are indeed described by the latter model.

We next address the question whether our first-order expansion around multi-kink configurations is a meaningful approach. First, we estimate second-order effects. To this end, we again consider the fluctuation with spatial size  $l$  and magnitude  $|\eta_l|$ . In this case, the ratio  $\delta^{(2)}E/\delta^{(1)}E$  of the second- and first-order corrections to the total energy can be expressed in terms of the renormalized frequency of the phonon with wave vector  $\pi/a$ . This frequency can be calculated in the two limiting cases for the on-site electron-electron interaction  $U$ , for which the dependence of the chain energy on the value of the dimerization is known:  $U = 0$  (SSH model) [1] and  $U \gg t_0$ , when the low-energy excitations are described by the spin-Peierls model [15]. We then find

$$\frac{\delta^{(2)}E}{\delta^{(1)}E} = \frac{\xi_0}{l} \begin{cases} \frac{1}{2}(1 - \lambda), & \text{for } U = 0, \\ \frac{1}{4}\gamma\lambda, & \text{for } U \gg t_0, \end{cases} \quad (12)$$

plus higher-order terms in powers of  $\xi_0/l$ . Therefore, our approach is valid as long as the average distance between the kinks is much larger than the correlation length (dilute gas of kinks).

Second, we should stress that, although the energies of the multi-kink configurations are calculated perturbatively, the stabilization of kinks by weak disorder is clearly a non-perturbative effect. In fact, as long as  $\delta^{(2)}E/\delta^{(1)}E \ll 1$ , a multi-kink lattice configuration is only slightly perturbed by disorder. Therefore, in this weak-disorder regime a uniformly dimerized lattice cannot evolve continuously into one containing kink-antikink pairs as a result of increasing disorder. Instead, the number of kinks in the minimal energy lattice configuration of a chain with disorder fluctuation of fixed shape,  $\Lambda\eta(x)$ , increases discontinuously by 2 when  $\Lambda$  passes the critical values, at which the energy of the chain with  $2(N+1)$  kinks drops below the energy of the same chain with  $2N$  kinks (cf. eq. (8) for  $N=0$ ). The crucial point is that these critical  $\Lambda$  values may occur in the regime where the total chain energy is still linear in  $\Lambda$ , as the first-order correction to the energy due to Gaussian disorder is proportional to the square root of the chain length.

Elsewhere [16], we show in detail that the estimate for the density of disorder-induced kinks eq. (11) is, in fact, the exact result in the limit where the average distance between kinks is much larger than the correlation length  $\xi_0$  (dilute gas of kinks) and much smaller than the length of the chain  $L$ . The exact solution was obtained by noticing that the disorder averaged free energy of the chain at sufficiently low temperature has the form of a matrix element of the Green function describing the relaxation of a spin  $\frac{1}{2}$  in a random magnetic field. The coordinate along the chain plays the role of the (imaginary) time in which the relaxation takes place, while the kinks correspond to spin-flips. The Green function was found by solving the corresponding Fokker-Planck equation.

We now discuss the consequences of the disorder-induced solitons for the optical and magnetic properties. In the absence of electron-electron interactions, the finite density of kinks leads to the appearance of a peak in the single-particle density of states at  $\varepsilon=0$ , because each kink carries an electron state with zero energy [1]. At weak disorder this peak is sharp since the distances between the kinks are large, so that the splitting of the energies of the electron states localized near different kinks due to their mutual interaction is very small ( $\sim \exp[-\frac{l}{\xi_0}]$ ). The peak in the density of states should result in a midgap peak in the optical absorption spectrum. In undoped trans-polyacetylene, however, this peak is not observed. This can be ascribed to a small magnitude of disorder, which is, however, unlikely, since the average (presumably disorder-limited) conjugation length of trans-polyacetylene is known to be of the order of several tens of carbon atoms [17].

The on-site Coulomb repulsion decreases the neutral soliton energy [7], [13] ( $\gamma < 1$ ), thus increasing the kink density (eq. (11)). However, at the same time, the Coulomb interaction shifts the absorption peak resulting from the neutral kinks towards higher energies, where it may merge with the peak resulting from interband transitions. This may explain the absence of a clear midgap peak in the absorption spectrum, but it does not reconcile the theory with magnetic measurements. The neutral disorder-induced kinks have spin  $\frac{1}{2}$  and should contribute to the magnetic susceptibility. However, the observed Curie susceptibility for undoped trans-polyacetylene corresponds to only one free spin per 3000 carbon atoms [18], which is much smaller than the average density of kinks given by eq. (11) for the disorder magnitude used in [9] to fit the absorption spectrum.

This contradiction between theory and experiment clearly poses questions as to the applicability of the SSH or the Peierls-Hubbard models to trans-polyacetylene. Here we note several factors that may solve this problem. First, interchain interactions counteract the formation of free kinks, binding them into pairs. Second, quantum lattice motion induces an effective

interaction between the spins of neighboring solitons, resulting in a spin-liquid with a singlet ground state. Finally, the free spins of solitons can be bound by chemical impurities. Further research is needed to see whether the quantitative effects of these factors are strong enough to account for the strong reduction in the number of observed free spins.

In summary, we have shown that in Peierls chains arbitrarily weak off-diagonal disorder induces a finite density of neutral solitons. As we discussed, these solitons strongly affect the observable properties of the chains. We believe that they also play an important role in the phase transition of disordered materials into the Peierls state.

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